

REMARKS

The Office Action of May 20, 2003 provides the examination of claims 1-8 and 10-26, claim 9 having been earlier canceled. Claims 16 and 22 are indicated as allowable if re-written into independent form incorporating any intervening claims. Applicants have so amended claims 16 and 22 herein.

Support for new claims 26 and 27 is found at page 7, line 3, of the specification.

Rejections under 35 U.S.C. § 112, second paragraph

Claims 23-26 stand rejected under 35 U.S.C. § 112, second paragraph, for allegedly being indefinite in the recitation of "a method according to claim 10", which is a composition claim. Claims 23 and 25 have been amended to recite dependence upon claim 18, thus overcoming this rejection.

Claim 18 is rejected under 35 U.S.C. § 112, second paragraph, for allegedly being indefinite in the recitation of a, "sufficient" time. The term "sufficient" is deleted, thus obviating this rejection.

Claim 25 is rejected 35 U.S.C. § 112, second paragraph, for allegedly being indefinite in the recitation of a "type" of viologen salt. This term is deleted, thus obviating this rejection. Further amendments are made to claim 25 to avoid possible problems of lack of antecedent basis.

Claim 26 35 U.S.C. § 112, second paragraph, for allegedly being indefinite in the recitation of, "whenever". This term is deleted, thus obviating this rejection.

Rejections over prior art

Natsuko et al.

Claims 1, 8, 10-15, 17-18, 21 and 26 stand rejected under 35 U.S.C. § 102(b) as being anticipated by Natsuko et al. JP 07-301828. This rejection is respectfully traversed. Reconsideration and withdrawal thereof are requested.

The Examiner characterizes Natsuko as disclosing a film of a polymer such as polyolefin or PTFE that has been sprayed with a solution or sol of a viologen derivative and dried. The Examiner notes a solid ion conductivity of the polymer of 1.5 to  $2.5 \times 10^{-4}$  S/cm. The Examiner further characterizes Natsuko as disclosing a dihalide derivative of a viologen.

Applicants submit that the Examiner misapprehends the disclosure of the Natsuko reference. In particular, Natsuko discloses a porous polymer film. Viologen is applied as an electrolyte and the application of the viologen results in droplets of the viologen being lodged in the pores of the polymer film (see, e.g. page four of the Examiner's translation of the reference). It is the viologen that is conductive, not the polymer. Accordingly, Natsuko fails to disclose a polymer

made conductive by reaction with the viologen and so fails to anticipate the instant invention.

The Examiner asserts that, if the claims are not anticipated by Natsuko, then they are obvious (35 U.S.C. § 103(a)). Applicants submit that Natsuko is not sufficient to establish *prima facie* obviousness of the invention, in that Natsuko does not disclose or suggest any reaction between the polymer and the viologen to render the polymer itself conductive. That the polymer itself becomes conductive is evidenced by the attached Exhibit 1, a publication by the inventors (B. Zhao et al., *Synthetic Metals* 123:263 (2001)), showing that the polymer retains conductivity even after the viologen solution has been washed away. 

Claims 1, 8, 15, 18 and 26 are rejected under 35 U.S.C. § 102(b) as being anticipated by Kumiko et al. JP 06-102540. This rejection is respectfully traversed. Reconsideration and withdrawal thereof are requested.

The invention as described in claims 1, 8, 15, 18 and 26 is not anticipated by Kumiko for the same reasons as these claims are not anticipated by Natsuko. That is, Kumiko also discloses the filling of the pores of a polymer film with a solution or sol of a viologen. (See, e.g., the abstract.) Again it is the viologen solution that provides conductivity. There is no change in the conductivity of the polymer itself as is recited

in the present claims. Thus, Kumiko does not anticipate claims 1, 8, 15, 18 and 26 so the instant rejection should be withdrawn.

Furthermore, Kumiko does not render the claimed invention *prima facie* obvious. Kumiko neither discloses nor suggests that any polymer can be made conductive by treatment with viologen.

Claims 1, 8 and 15 are rejected under 35 U.S.C. § 102(b) or 35 U.S.C. § 103(a) as being anticipated by, or obvious in view of Sammells '817. This rejection is respectfully traversed. Reconsideration and withdrawal thereof are requested.

Sammells discloses an electrochromic cell in which a "polymer electrolyte" constituted by an ionically conductive polymer filled with a supporting electrolyte is used. The "polymer electrolyte" of Sammells is in effect an ion exchange resin immersed in a salt solution. (See, e.g. col. 4 and esp. lines 50 ff.) In contrast, the invention described by claims 1, 8 and 15 is an electrically conductive polymer made by treatment of a polymer with a viologen salt. As explained above, the polymer of the invention is able to conduct even in the absence of the viologen, a property not exhibited by the ionically conductive polymers of Sammells. Thus, Sammells does not anticipate the present invention and the instant rejection should be withdrawn.

Also, the claimed invention is not *prima facie* obvious in view of Sammells, as Sammells fails to disclose or suggest any polymer made to be electrically conductive by treatment with a viologen salt.

Claims 1-8, 10-15, 17-21 and 24-26 stand rejected under 35 U.S.C. § 102(b) or 35 U.S.C. § 103(a) as anticipated or obvious over Allemand et al. '717. This rejection is respectfully traversed. Reconsideration and withdrawal thereof are requested.

Allemand describes an electrochromic cell. Allemand's cell is one that has an "electrochemically active layer of polyaniline or a polyaniline derivative" and an electrolyte containing a viologen salt. Thus, Allemand discloses a layered structure comprising a layer of polyaniline and a layer of a viologen salt or solution thereof. Allemand does not disclose any polymer made electrically conductive by treatment with a viologen salt.

In the case of Allemand, the object is to prepare an electrochromic device with an electrochemically active material which can be reduced or oxidized without a separate processing step. The most preferred device has an electrochemically active layer of polyaniline and an electrolyte containing viologen salt. An effective amount of reducing or oxidizing agents is incorporated to achieve the desired reduction or oxidation of

the electrochemically active material. Heat or radiation may be applied out to assist the process. The invention of Allemand is not relevant to the present application since the object of Allemand is to oxidize or reduce the polyaniline. The changing of the polyaniline between the different oxidation states, emeraldine and leucoemeraldine, results in a color change which is desired for Allemand's device but does not confer conductivity to the polymer.

As Allemand does not disclose or suggest any polymer made conductive by treatment with a viologen salt, the invention as recited in claims 1-8, 1-15, 17-21 and 24-26 is not anticipated by the reference nor obvious in view of it. Accordingly, the instant rejection should be withdrawn.

Claims 1-8, 10-15, 17-21 and 24-26 stand rejected under 35 U.S.C. § 103(a) as obvious over Sammells or Allemand et al. in view of Yu et al. '338. This rejection is respectfully traversed. Reconsideration and withdrawal thereof are requested.

The disclosures of the Sammells and Allemand are explained above. The Examiner cites Yu as disclosing viologen dihalide salts.

As explained in detail above, neither Sammells nor Allemand disclose or suggest any polymer made to be electrically conductive by treatment with a viologen salt. Yu also fails to

disclose or suggest this feature of the claimed invention and therefore the combinations of references asserted by the Examiner fails to include a feature recited in the claims. Accordingly, the combined references fail to establish *prima facie* obviousness of the invention and the instant rejection should be withdrawn.

Applicants submit that the present application well describes and claims patentable subject matter. The favorable action of withdrawal of the standing rejections and allowance of the application is respectfully requested.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Mark J. Nuell (Reg. No. 36,623) at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By Mark J. Nuell  
Mark J. Nuell, #36,623

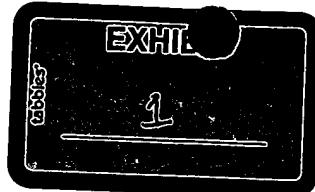
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## Interactions between polyaniline and viologens

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### Abstract

The interactions between polyaniline (PANI) and viologen solutions were investigated. The changes in the structure of PANI were monitored using X-ray photoelectron spectroscopy (XPS) and UV-VIS absorption spectroscopy. The results indicated that electron transfer from PANI to viologen occurs readily, resulting in the formation of positively charged nitrogen species in the PANI. This is accompanied by an increase in conductivity of the PANI, together with a transfer of halogen anions from the viologen to PANI. Dissolved oxygen appears to play an important role in these interactions. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Polyaniline; Viologen; Doping; Electron transfer

### 1. Introduction

The aniline family of polymers has been known for almost a century and has continued to attract considerable interest due to its electroactive nature and its wide range of potential applications ranging from corrosion inhibition [1] to sensors [2,3]. The polymers are basically poly(*p*-phenyleneimineamine)s in which the oxidation state can be varied from the fully reduced, leucoemeraldine (LM) to the fully oxidized pernigraniline (PNA). The 50% intrinsically oxidized form or emeraldine (EM) is the most commonly studied. The electrical conductivity of EM base can be increased by more than 10 orders of magnitude upon treatment with protonic acids [4]. Under such circumstances, the imine nitrogens are preferentially protonated [5]. In the case of LM, the effect of protonic acid treatment on electrical conductivity is significantly less than that observed with EM [6]. However, LM can also undergo oxidative doping by proton-free electron acceptors such as halobenzoquinones to result in a conductive state [7]. Another class of compounds that readily undergoes electron transfer is the viologens, which is more formally known as 1,1'-disubstituted 4,4'-bipyridinium ions. These compounds have electrochemically and photochemically reversible properties and interesting behavior in different oxidation states. While viologens are known to readily

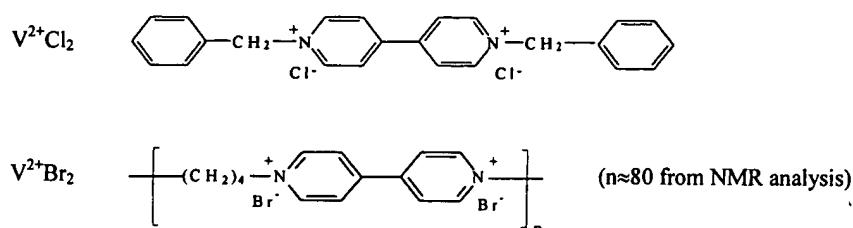
undergo redox reactions [8], interactions between polyaniline (PANI) and viologens have not been studied. In the present work, we report on the interactions between PANI and viologens in water. These interactions result in the conversion of EM base and LM to the doped state. The resulting structural changes of the PANI are followed using UV-VIS absorption spectroscopy and X-ray photoelectron spectroscopy (XPS).

### 2. Experimental

PANI was synthesized via the oxidative polymerization of aniline with ammonium persulfate in 0.5 M H<sub>2</sub>SO<sub>4</sub> according to the method described in the literature for 1 M HCl [9]. It was converted to EM base by treatment with excess 0.5 M NaOH for 24 h. Freestanding EM base films of about 10–20 μm in thickness were prepared by casting from *N*-methyl-2-pyrrolidinone (NMP) solutions containing 5% by weight of EM base. EM coatings on low density polyethylene (LDPE) substrates were synthesized as follows: the LDPE substrates (0.125 mm in thickness) were first treated with O<sub>2</sub> plasma for 60 s, and then immersed in the polymerizing solution of aniline for 2 h. The coating was then undoped by treatment with 0.5 M NaOH for 1 h. LM was prepared by treating EM base film or coating with 10 vol.% hydrazine for 48 h.

Two kinds of viologens (denoted as V<sup>2+</sup>Cl<sub>2</sub> and V<sup>2+</sup>Br<sub>2</sub> with structures shown below) were prepared according to the method reported in [10].

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Solutions of viologens of different concentrations (based on the content of the bipyridinium ion units) were prepared by dissolving the viologen in deionized water. The PANi films were immersed in excess viologen solutions (where the bipyridinium ion units  $\gg$  the aniline units) for fixed periods of time. The samples were rinsed with deionized water and dried under reduced pressure before being characterized.

The electrical conductivity of the PANi films after treatment with viologen solutions was measured by the two-probe method and reported as the sheet resistance ( $R_s$ ) in  $\Omega/\text{sq}$  [11]. The changes in the electronic spectrum of the PANi coating on LDPE as a result of the interactions with viologens were monitored using an UV-VIS-NIR scanning spectrophotometer (Shimadzu UV-3101PC), with pristine LDPE film as the reference. FTIR absorption measurements were carried out on a BIO-RAD FTS135 spectrometer while the surface compositions were measured using XPS according to the method described in previous publications [7,12].

### 3. Results and discussion

It was found that when freestanding EM base films were treated with viologen in water, the base films turned from brown to blue and the films became electrically conductive. Fig. 1 shows how the sheet resistance,  $R_s$ , decreases with the treatment time in viologen solutions of different concentrations. It can be seen that the rate of change and the level of conductivity achievable are highly dependent on the concentration of viologen and the type of viologen molecules. The  $R_s$  achievable when EM films were treated with 0.24 M  $\text{V}^{2+}\text{Cl}_2$  solution is as low as  $1.2 \times 10^4 \Omega/\text{sq}$ , which is about one order of magnitude higher than when EM is treated with  $\text{HClO}_4$  of similar concentration.

The conversion of the PANi from the neutral base state to the conductive (doped) state is also readily seen by monitoring the UV-VIS absorption spectra of the PANi coating on LDPE films after treatment with the viologen solution (Fig. 2). For LM treated with viologen, it can be seen that with time the spectrum shows an increase in intensity in the 630 nm region, together with a new band at 430 nm and a broad absorption band in the 800–1000 nm region (Fig. 2(a)). The former is characteristic of the imine ( $-N=$ ) groups while the latter two features are characteristics of the doped PANi [13]. These results suggest that the interaction of LM with viologen result in the oxidation of some amine ( $-NH-$ ) groups to imine groups and also in the doping of the polymer as well. The possible mechanisms for LM to be

doped through interactions with viologens are depicted in Scheme 1. The exposure of EM base coating on LDPE to the viologen solution resulted in a very rapid color change of the film from blue to green. This is illustrated by Fig. 2(b), where the rapid disappearance of the 630 nm band and the rise in the 430 nm band and the absorption tail beyond 800 nm are consistent with the conversion of the imine units in EM base to the positively charged species of the EM salt. The interaction of EM base with viologen is probably initiated by the electron transfer from EM to the viologen to result in cation radicals of the form of  $=\text{N}^{\bullet+}-$ . A comparison of the spectra in Fig. 2(a) and (b) indicates that the conversion of the base form of PANi to the doped state is much more rapid when the  $-\text{N}=$  groups are available to participate in the electron transfer to viologen. A comparison of the FTIR absorption spectra of the EM base coating on LDPE film before and after treatment with the viologen solution shows an increase in intensity and significant broadening of the  $1140 \text{ cm}^{-1}$  band in the latter. This is consistent with the conversion of the EM base to a doped and conductive state [14,15].

The XPS N 1s core-level spectra of the PANi samples before and after treatment with viologen were deconvoluted using previously established peak assignments for  $\text{-N=}$ .

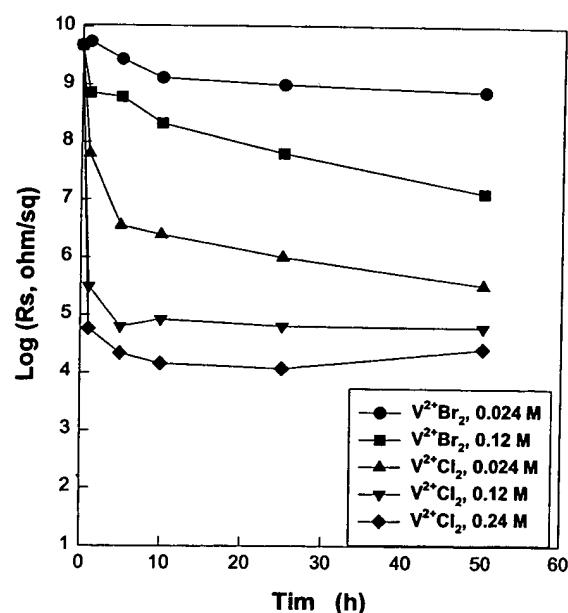


Fig. 1. Sheet resistance ( $R_s$  in  $\Omega/\text{sq}$ ) of EM base films after treatment with viologen solutions in air for varying periods of time.

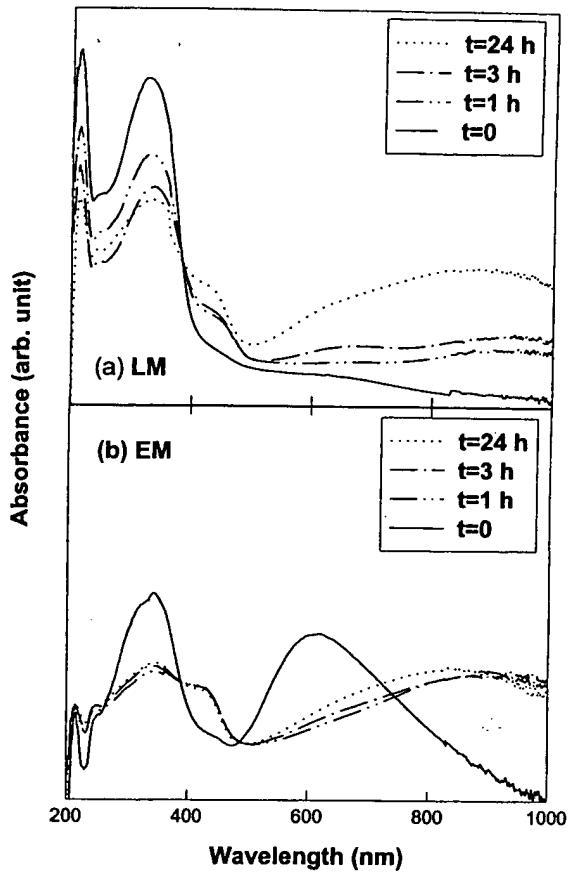


Fig. 2. UV-VIS absorption spectra of (a) LM and (b) EM coatings on LDPE after treatment with viologen solution ( $0.024\text{ M }V^{2+}\text{Br}_2$ ) in air for varying periods of time.

$-\text{NH}-$  and  $\text{N}^+$  species [13], shown in Fig. 3. It can be seen that for both LM and EM, there is an increase in the proportion of positively charged nitrogen after viologen treatment. However, in the case of LM, this increase is accompanied by a decrease in the proportion of the  $-\text{NH}-$  groups whereas for EM, the proportion of  $-\text{N}=$  groups is observed to decrease. This observation is consistent with the proposed difference in the type of cation radicals formed during the interaction

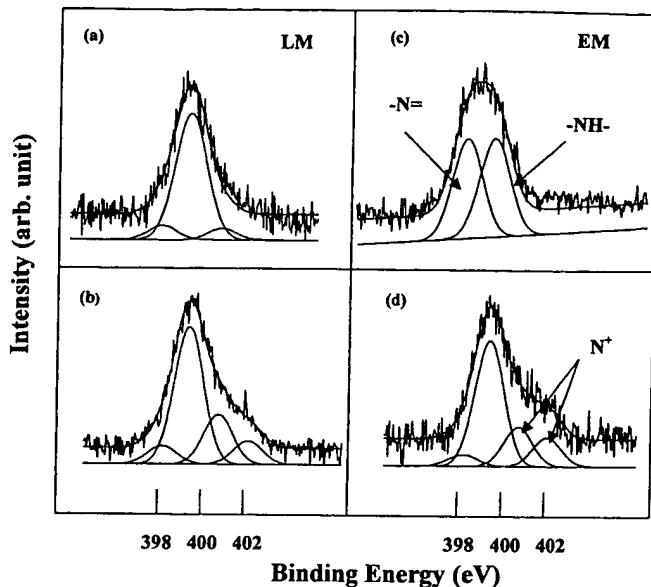
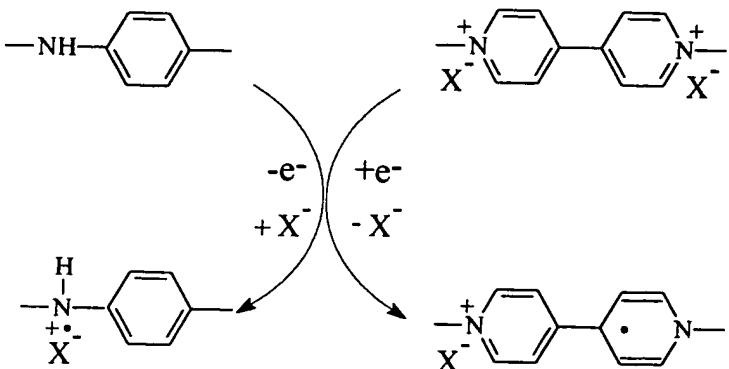


Fig. 3. N 1s core-level spectra of (a) LM; (b) LM treated with  $0.24\text{ M }V^{2+}\text{Cl}_2$  for 24 h; (c) EM base and (d) EM base treated with  $0.24\text{ M }V^{2+}\text{Cl}_2$  for 24 h.

of LM and EM with viologen. From the deconvoluted Cl 2p core-level spectra, it was concluded that only the chloride anion,  $\text{Cl}^-$  ( $\text{Cl } 2p_{3/2}$  at 197 eV), was present on the LM and EM films after treatment with  $V^{2+}\text{Cl}_2$ .

The viologen radical cation is sensitive to oxidation and it can easily and rapidly transfer electrons to dissolved oxygen, forming  $\text{O}_2^-$  and possibly other anions while itself reverts back to the salt state [16–18], as shown in Scheme 2. The importance of the role of dissolved oxygen is clearly illustrated by comparing the above results (Fig. 2) with those obtained when a thoroughly degassed viologen solution is used in the experiment. In the latter case, no band at 800–1000 nm appears in the UV-VIS absorption spectra of the EM coating (Fig. 4) even after 40 h of treatment with  $0.024\text{ M }V^{2+}\text{Br}_2$ , suggesting that the interactions of viologens with EM base is retarded in the absence of  $\text{O}_2$ .



Scheme 1.

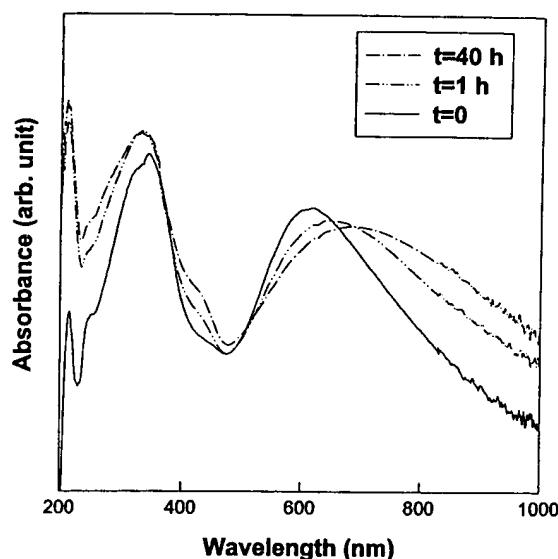
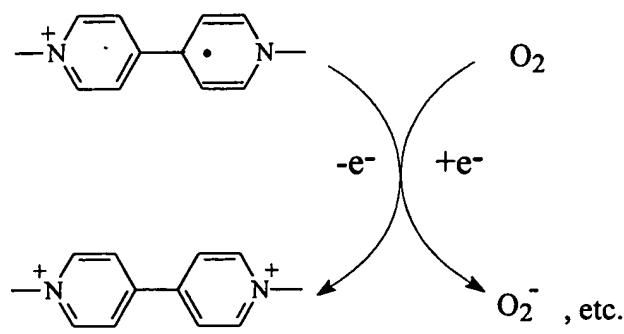


Fig. 4. UV-VIS absorption spectra of EM coating on LDPE after treatment with viologen solution ( $0.024\text{ M }V^{2+}\text{Br}_2$ ) in an argon atmosphere.

#### 4. Conclusion

The present study reveals the interesting interactions between PANi base and viologens in water. These interac-

tions result in the conversion of PANi base to the doped state. The reactions are initiated by electron transfer from the nitrogen in PANi to the viologen, resulting in the formation of positively charged nitrogen species in the former. The halogen anions associated with the viologens are in turn transferred to PANi. In the absence of dissolved oxygen, these reactions are severely retarded. Further work is in progress and the detailed results will be reported in a subsequent publication.

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**Abstract**

The interactions between polyaniline (PANI) and viologen solutions were investigated. The changes in the structure of PANI were monitored using X-ray photoelectron spectroscopy (XPS) and UV-VIS absorption spectroscopy. The results indicated that electron transfer from PANI to viologen occurs readily, resulting in the formation of positively charged nitrogen species in the PANI. This is accompanied by an increase in conductivity of the PANI, together with a transfer of halogen anions from the viologen to PANI. Dissolved oxygen appears to play an important role in these interactions.

**Author Keywords:** Polyaniline; Viologen; Doping; Electron transfer

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